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CRYSTALLIZATION OF SiO_2 FROM ETHYLSILICATE-BASED GELS

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The mechanism of polymerization of ethylsilicate gels catalyzed by hydrochloric, nitric, and orthophosphoric acids is studied. The effect of the ethylsilicate : water ratio in the hydrolyzate on the phase composition and the optical properties of the heat-treated powder is investigated. The synthesis of opal is registered in heat treatment of ethylsilicate gels, and an explanation for the mechanism of its formation is proposed. It is demonstrated that the formation of the opal structure in gels delays the crystallization of cristobalite in heat treatment.

A widely known fact is the use of composite materials based on medicinal plastics and fine ceramic fillers with large specific surface area in dentistry, and most frequently such fillers are made of glasses. The complex composition of glass makes it possible to obtain in a powder the refractive index corresponding to the refraction of light by the polymer matrix. When the refractive indexes of the matrix and the filler differ even by 0.01, the clarity of the composite material is sharply deteriorated, which complicates its use as dental filling, due to aesthetic considerations. A required refractive index in the filler can be most easily accomplished by adjusting its composition in the course of glass melting. However, this method has a significant disadvantage: the high glass-melting temperatures and even more so the lengthy milling process make this method too energy-consuming.

The use of sol-gel technology makes it possible to decrease the heat treatment temperature (to less than 1000°C) and exclude lengthy milling in the development of finely dispersed powders of preset compositions. Therefore, the sol-gel technology is the simplest and the most promising technology for the production of fine siliceous fillers for dental plastics.

The purpose of the present work was to study the processes of crystallization of silica from hydrogels based on ethylsilicate-32, which was hydrolyzed in the presence of various catalysts with different ratios between ethylsilicate and water.

The gels were studied by infrared spectroscopy employing a UR-20 spectrophotometer in the range of 400 – 4000 cm^{-1} , using single-crystal potassium bromide as the reference standard.

The phase composition of the heat-treated powders was determined using a DRON-3 x-ray diffractometer with CuK_α radiation, as well as by the petrographic method using an MIN-8 optical microscope.

It is known that the pH of silicic acid sol has an effect on the mechanism of polycondensation and, accordingly, on the life term of sol and on the size of its particles. The shape of the emerging polymer molecules depends on the quantity of water taken for ethylsilicate hydrolysis [1]. With low pH values (< 2.5) and the water : alcohol ratio lower than the stoichiometric ratio, linear polymers emerge, which can then form lateral bonds and cross-link to each other, thus forming gel. This agrees with the data in [2, 3], which also identified the formation of linear polymers under the specified conditions.

With an elevated water content and a low pH value, ethylsilicate is hydrolyzed and forms silicic acid [1]; however, the mechanism of its polymerization is not quite clear, i.e., it is not certain whether weakly bonded linear polymers are formed or spheroid colloid particles. The authors of [2] believe that such colloid solutions behave similarly to hydrolyzate obtained in the presence of NH_4OH , i.e., form spheroid and colloid polymers.

The published data do not clarify whether the alcoholate : water ratio affects the phase composition of the heat-treated powder. Therefore, the present investigation considered acid hydrolyzates of ethylsilicate-32, varying the ethylsilicate : water ratio from 65 : 35 to 88 : 12. Hydrochloric, nitric, and orthophosphoric acids used as catalysts in the hydrolysis of ethylsilicate, were taken in the amount which made the pH of the solution equal to 1 – 2.

It is known that the reaction of ethylsilicate hydrolysis is not fully completed, since the process of polymerization and

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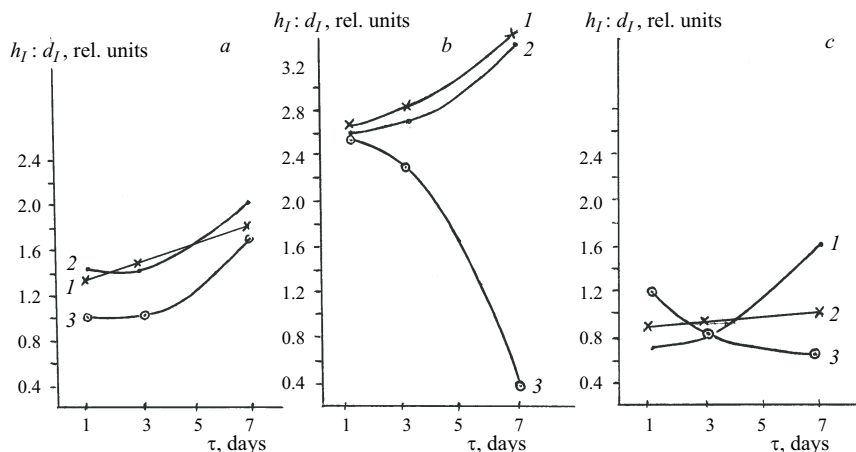


Fig. 1. Variations in intensity of characteristic bands in IR spectra of ethylsilicate gel depending on their aging period: *a*, *b*, and *c*) 950 cm^{-1} (ν_s is Si–OH), 1090 cm^{-1} (ν_s is Si–O), and 800 cm^{-1} (ν_{as} is Si–O), respectively; catalysts of ethylsilicate hydrolysis: 1) HCl, 2) HNO_3 , 3) H_3PO_4 .

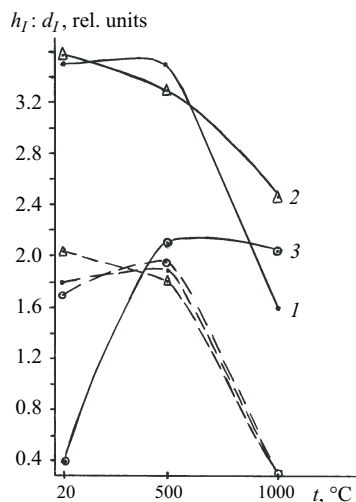


Fig. 2. Variations in intensity of characteristic bands in IR spectra of ethylsilicate gel depending on their heat treatment temperature: solid curves) 1090 cm^{-1} , dashed curves) 950 cm^{-1} ; catalysts of ethylsilicate hydrolysis: 1) HCl, 2) HNO_3 , 3) H_3PO_4 .

polycondensation of the forming silicic acid begins at the same time. In the course of sol aging, the reactions of hydrolysis and polycondensation continue, facilitating the growth of the main chains of polymer molecules and their cross-linking by lateral bonds [4].

The study of the infrared absorption spectra revealed the presence of polysilicic acid in all gels (bands at 470, 800, 950, and 1090 cm^{-1}). In using nitric and hydrochloric acid, the rate of polycondensation of silicic acid exceeds the rate of hydrolysis of tetraethoxysilane; therefore, such gels, in addition to polysilicic acid, contain small quantities of polyethoxysilanes (the band $1350 - 1450\text{ cm}^{-1}$).

The molecular water released in polycondensation participates in the hydrolysis of the remaining ethoxy groups in polyethoxysilanes, as a consequence of which ethyl alcohol dissolves in the intermicelle medium, and the newly formed silanol groups are registered in the IR spectra through an insignificant increase in the intensity of the band of valence vibrations of the Si–OH bond at 950 cm^{-1} (Fig. 1*a*) and the simultaneous decrease in the intensity of the band at $1350 - 1450\text{ cm}^{-1}$, correlated with polyethoxysilanes.

The arising silanol groups $\equiv\text{SiOH}$, both surface and intraglobule ones, easily form a hydrogen bond between each other, especially if these atoms are arranged near the same silicon atoms or near two adjacent silicon atoms [5]. These silanol pairs disturbed by the hydrogen bond can easily condense and form $\equiv\text{Si-O-Si}\equiv$ bridges, which is registered on the spectra by the increased intensity of the bands of valence vibrations of $\equiv\text{Si-O}$ bonds.

It is known that lengthening of a siloxane chain is accompanied by an insignificant decrease in the intensity of the band at 1090 cm^{-1} , which at the same time becomes wider. In spite of the fact that the form of the band on the IR spectrum depends on several factors [6, 7], in this particular case, a modification of the ratio between the height and the half-width of the band 1090 cm^{-1} can be taken as an indirect characteristic of the process of polycondensation of silicic acid, which is accompanied by the growth of the $\equiv\text{Si-O-Si}\equiv$ chain. As the aging period of gels containing hydrolysis catalysts HCl and HNO_3 increases, the process of the formation of $\equiv\text{Si-O-Si}\equiv$ bridges starts prevailing over the chain extension, which is manifested in the plot by the increased ratio $h_I : d_I$ (Fig. 1*a*, *b*, and *c*).

The use of ethylsilicate of orthophosphoric acid (which is water-removing) in the capacity of hydrolysis catalyst results in the formation of longer siloxane chains, which causes an abrupt decrease in the ratio $h_I : d_I$.

The heat treatment of gels at temperature 500°C facilitates the complete decomposition of polyethoxysilanes, which is indicated by the disappearance of the band $1350 - 1450\text{ cm}^{-1}$, and decomposition of polysilicic acid, which is accompanied by the decreased intensity of the band at 950 cm^{-1} (Fig. 2). The active dehydroxylation of silanol pairs disturbed by the hydrogen bond, with the heat-treatment temperature increasing up to 1000°C , facilitates a significant extension of siloxane chains in gels with nitric and hydrochloric acids, which leads to a sharp decrease in the ratio $h_I : d_I$. A different shape of the curve reflecting the decomposition of gel with orthophosphoric acid is presumably due to the splitting effect of the phosphate anion on the $\equiv\text{Si-O-Si}\equiv$ bonds in heat treatment [8].

Thus, the heat treatment at 1000°C leads to the decomposition of ethylsilicate gels to amorphous silica (the bands 470, 800, and 1090 cm⁻¹), which is substantiated by the x-ray phase and petrographic analysis. Only a long exposure (2–3 h) at temperature 1000°C initiates crystallization in silica, and the diffraction pattern exhibits weak diffraction maximums corresponding to cristobalite. At temperature 1200°C, the process of the crystallization of cristobalite becomes significantly activated, which is accompanied by a sharp increase in the intensity of the cristobalite peak ($d = 4.08$ nm).

The petrographic analysis of the powders heat-treated at temperatures below 1000°C shows the presence in immersion specimens of an isotropic phase, whose refractive index in different powder samples varies from 1.400 to 1.460. It was observed that the refraction of light in powders is directly proportional to the ethylsilicate : water ratio and is equal to 1.429 for the ratio 65 : 35 and 1.462 for 88 : 12. As the temperature of heat treatment of gels grew to 1200°C, an anisotropic phase with the refractive index 1.482 became predominant in the powder, which correlates with the light refraction in β -cristobalite ($d = 4.08$ nm). On mixing these powders together with acrylate oligomer with the respective refractive index, the mixture had weak opalescence.

All this suggests that the powders contain opal, which is an amorphous variety of silica with the formula SiO₂ · n H₂O and refraction of light within the limits of 1.400–1.460. The amount of water in opals varies from 5–9 to 28%, and less frequently to 34%. Although opal is amorphous, it is proved to possess an ordered structure consisting of densely packed silica globules arranged in accordance with hexagonal and (or) cubic packing. The empty space between the globules is occupied by air or water, and as the water content increases, the refractive index of the opal decreases.

The formation of opal in heat treatment of ethylsilicate gels can be explained as follows. Gel as a cohesive-disperse system consists of a dispersed phase (SiO₂ colloid particle aggregates) and a dispersion medium (in our case this is an aqueous solution of alcohol formed in hydrolysis and the acid which is the catalyst of ethylsilicate hydrolysis), which partly evaporates in the course of gel maturing. In the course of "recondensation" of the primary colloid particles on colloid aggregates, the latter become subjected to osmotic pressure, which develops the hydrostatic compression of the aggregates [9]. Under heat treatment, this pressure impedes the release of molecularly adsorbed water and intraglobule silanol groups from the intraglobular space of colloid aggregates, as a consequence of which the powder formed after heat treatment contains both structurally fixed and (in small quantities) adsorbed water, which delays the crystallization of cristobalite.

Assuming that the synthesis of cristobalite can be initiated by water removal, cross-linked hydrogel was destroyed by dispersing it in water and thus increasing the specific surface area of the colloid silica globules. By means of decant-

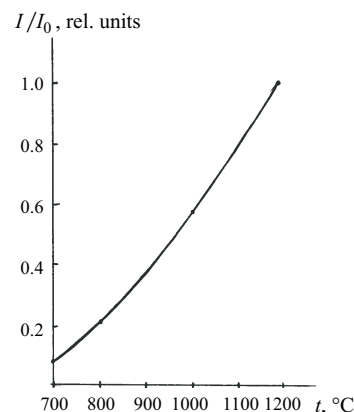


Fig. 3. Cristobalitizing of powders in heat treatment.

ing, the pH of the refined solution in the obtained suspension was brought to 6–7, and then the suspension was centrifuged and dried. The cristobalitizing of these powders in heat treatment started already at 700°C, was intensified with a further temperature rise, and reached its maximum value at 1200°C (Fig. 3).

Thus, the formation of opal from sol-gel compositions based on ethylsilicate was identified. The ethylsilicate : water ratio affects the diffraction of light in heat treated amorphous siliceous powder but does not modify its qualitative composition. The presence of structurally fixed water in siliceous powder delays the crystallization of cristobalite.

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